

## **Possible Jahn-Teller effect and strong electron-phonon coupling in beryllium hydride**

Ivan Bozovic

Brookhaven National Laboratory, Upton, NY 11973, USA

Abstract. Possibility of Jahn-Teller effect in extended systems, such as polymers and quasi-one-dimensional metals, is discussed using beryllium hydride as an example. If this polymer compound could be made metallic by doping (e.g., with Lithium), we conjecture that it should show strong-electron phonon coupling and possibly superconductivity with a relatively high critical temperature.

### **1. Introduction: K. A. Mueller and Jahn-Teller bipolarons**

As we all know, the search and the discovery of high-temperature superconductivity (HTS) in cuprates<sup>1</sup> was guided by Karl Alex Müller's thinking about Jahn-Teller effect (JTE) and strong electron-phonon coupling. Imagine an isolated ionic cluster with a  $\text{Cu}^{2+}$  cation sitting at the center of an octahedral cage comprised of six  $\text{O}^{2-}$  anions. If the highest occupied one-electron state of this complex can be identified with the half-filled  $\text{Cu } 3d^9$  state, one would expect the octahedron to distort as the result of JTE. This indeed could cause strong coupling between the electrons and the ionic displacements. Strong electron-phonon coupling has been traditionally related to a 'high'  $T_c$  according to the standard BCS theory. Whether this reasoning really applies to cuprates is debatable; but (to quote D. Pavuna) what will be remembered after all these debates about HTS have long faded out is that Alex and George discovered the phenomenon in 1986. My understanding is that Alex actually still believes that in cuprates JTE is operational and leads to formation of bipolarons which Bose-condense into the HTS state.<sup>2,3</sup> Thus it seems appropriate in the Festschrift honoring his 80<sup>th</sup> birthday to talk about JTE, strong electron-phonon coupling, and superconductivity, from my personal angle. I hope this will find at least one interested reader - although knowing him (i.e, Alex) I am certainly ready for criticism. In any case, here is my offering.

### **2. Superconductivity in hydrides**

The quest for high-temperature superconductivity (HTS) has been a passion of numerous experimentalists and theorists for many years. One of the earliest candidate materials has been metallic hydrogen. Already in 1935, Wigner predicted<sup>4</sup> that molecular hydrogen, which at low temperature is an insulator, would turn metallic (and mono-atomic) under high-enough pressure,  $p > p_c = 25$  GPa. This prediction has been revisited subsequently by other prominent theorists including A. Abrikosov, N. Aschcroft, Yu. Kagan, etc., who calculated<sup>5-7</sup> much higher critical pressure - as high as 1,500 GPa. In 1968, Aschcroft raised the stakes further by predicting<sup>6</sup> boldly that metallic hydrogen would turn superconducting at  $T_c \sim 200$  K. I was not around at that time, but I guess that this must have caused consternation. This was an order of magnitude larger than the highest  $T_c$  found in any superconductor known at that time. It was also much higher than what was widely believed to be the theoretical limit, largely under the influence of W. McMillan

and some other leading theorists. One of their key arguments was that very strong electron-phonon coupling should inevitably cause lattice instability and distortion. On Aschcroft's side was the fact that hydrogen has the smallest mass and hence the highest Debye temperature - and his calculations. So far, we only know with certainty that his prediction about a very high critical pressure was most probably correct - as far as I know  $p_c$  has never been reached experimentally. [At least not for solid hydrogen - liquid hydrogen apparently can become metallic under shock compression.<sup>8</sup>]

This makes one turn attention to metallic hydrides. Here, experimentalists had better luck. Palladium hydride, PdH, was found to be superconducting at a respectable  $T_c = 8.8$  K, even though pure elemental Pd is not superconducting, not even under high pressure. Even more interesting, PdH showed a negative hydrogen isotope effect:  $T_c = 10.7$  K in PdD. Still further increase was achieved by Cu doping:  $T_c = 16.6$  K in  $\text{Pd}_{1-x}\text{Cu}_x\text{H}$ . This was rather interesting *per se* but it did not look like a big step in the quest for HTS.

However, in 1986, Overhauser predicted<sup>9</sup> that  $\text{LiBeH}_3$  and/or  $\text{Li}_2\text{BeH}_4$  may be metallic and show HTS such as it was envisioned for metallic hydrogen. This stirred a lot of interest. One of his statements, that these two compounds have modified-perovskite crystal structure, has been questioned and criticized,<sup>10</sup> primarily because his conclusions were based on rather poor experimental diffraction data showing just a dozen powder reflections.<sup>11</sup> Much more work followed, theoretical and experimental,<sup>12-19</sup> and now it appears that neither  $\text{LiBeH}_3$  nor  $\text{Li}_2\text{BeH}_4$  are metallic, much less superconducting. There was one glitch in late 1996, when all the daily news disseminated the Reuters announcement of a sensational discovery of superconductivity at  $T = 350$  by K S. Contreras and J-P. Bastide at the National Institute of Applied Science in Lyon, France. The alleged room-temperature superconductor was powder composed of Li, Be, and H. However, this result<sup>20</sup> could not be reproduced and was eventually dismissed by the scientific community.<sup>21</sup> So, the quest for HTS in hydrides is still open to anyone with courage (and resources) to try. Additional motivation can be found in more recent work of Aschcroft,<sup>22-25</sup> who has persisted at the forefront of theoretical research on possible hydrogen superconductivity till this days.

### **3. Vibronic coupling in 0D: the Jahn-Teller effect**

The Jahn-Teller theorem has the unfortunate reputation of being the most misinterpreted result in physical sciences. [For the clearest account see e.g. Englman's book.<sup>26</sup>] Actually, in its simplest version, the statement is almost trivial. If one assumes a molecule (or an ionic cluster) to have some symmetric structure, determines its electronic spectrum by a quantum-chemical calculation, and finds that the highest occupied one-electron level is degenerate and partially occupied, the original structure actually must be unstable with respect to a distortion that removes the degeneracy.

To see this, let us denote by  $|e\rangle$  and  $|e'\rangle$  the two degenerate molecular orbitals that correspond to the highest occupied one-electron level, and let the molecule be subject to a small asymmetric distortion of magnitude  $Q$ . In the first-order perturbation theory, the level will split into two, one level going down in energy and the other one going up. If the original degenerate level was occupied by a single electron - I am ignoring the spin for simplicity - the total electron energy will be reduced by  $\Delta E = \langle e' | Q \partial V / \partial Q | e \rangle$  which is linearly proportional to  $Q$ . The elas-

tic deformation of the molecule will cost some energy proportional to  $Q^2$ . The total energy will thus have the minimum at some  $Q_{\min} \neq 0$ . Jahn and Teller actually went one step further: for every possible molecular symmetry (described by the point group  $\mathbf{P}$ ), they identified the (symmetry of) active distortions. Now, contrary to what has been stated even in many textbooks, this does not mean that the molecule will simply distort statically. Rather, the total energy will have multiple (symmetry-related) minima with equal probability of occupancy, and the molecule will tunnel from one to another.<sup>26</sup> The overall  $\mathbf{P}$  symmetry of the (vibronic) Hamiltonian must be preserved!

#### **4. Vibronic coupling in 1D: the Peierls instability**

Let us turn now to the simplest translation-symmetric system, a periodic linear chain of atoms, each contributing a single atomic orbital  $|e\rangle$ . Let us assume that these orbitals have a significant overlap  $\mathcal{O} = \langle e' | e \rangle$ , so that the hopping integral  $t = \langle e' | H | e \rangle$  is large enough (specifically,  $t \gg kT$ ). This gives the electron band  $\varepsilon(k) = 2t \cos(ka)$ . The electron states are extended Bloch waves,  $\psi(k) = u(k) \exp(ikx)$ . If the band is partially occupied, the chain is metallic. The simplest case occurs when each atom contributes one electron. The band is half-filled; the Fermi level is found at  $k_F = \pi/2a$ . In this case, the matrix element of linear vibronic coupling,  $\langle \psi(-k_F) | \partial U / \partial Q | \psi(k_F) \rangle$ , is nonzero for  $Q = 2k_F = \pi/a$ . The chain is unstable against dimerization, since  $Q = \pi/a$  corresponds to the wavelength  $a' = 2a$ . This is the well-known Peierls instability.

The above phenomenon, the Peierls Effect (PE), is closely related to JTE, since both are electronic instabilities driven by the degeneracy of the relevant one-electron states, namely the HOMO levels  $|e\rangle, |e'\rangle$  in JTE and the Fermi level states  $\psi(k_F), \psi(-k_F)$ , in the Peierls model. However, there is a profound difference: JTE is a strong instability in the sense that the total electron energy reduction is linear in  $Q$ . In contrast, Peierls instability is a much weaker one, because in that case for a small distortion  $Q$  only the few states very close to  $E_F$  (within some range  $\Delta E \ll E_F$ ) are perturbed, since the Fermi statistics and Pauli principle do not allow the electrons to crowd very much. The total electron energy reduction in PE is  $\Delta E \sim Q^2 \ln Q$ . The point is that while both JTE and PE originate in linear vibronic coupling, they are qualitatively different in the sense that JTE is a strong (linear) instability while PE is a weak (logarithmic) one.

#### **5. The (absence of) JTE and PE in higher dimensions**

In real 3D crystals, one in general does not expect JTE instability because systematic degeneracy only occurs at some special (high-symmetry)  $k$ -vectors, which however form a ‘subset of measure zero’ within the set of all possible  $k$ -vectors, and generally don’t count for much at all.<sup>26</sup> The asymmetric ones, having no non-trivial point group symmetry, grossly outnumber the special ones. To say it more technically, irreducible representations of the relevant symmetry group (the crystallographic space group that leaves the  $k$ -vector invariant) are one-dimensional for every general  $k$ -vector. So there is simply no band degeneracy – except at few irrelevant points.

If the crystal is metallic, there will be so-called *star* degeneracy, i.e., there will be several states at the Fermi level connected by point-group symmetry of the corresponding wave-vectors. For example, in a tetragonal crystal, in the plane perpendicular to the rotation symmetry axis  $C_4$ , the four states  $\psi(\mathbf{k}_F), \psi(C_4\mathbf{k}_F), \psi(C_2\mathbf{k}_F), \psi(C_4^{-1}\mathbf{k}_F)$  must be degenerate. This degeneracy is similar to

what we had in the PE case described in Section 3. The difference here is that for a general shape of the Fermi surface, if we allow the crystal to distort along  $\mathbf{Q} = 2\mathbf{k}_F$ , this will reduce the energy of the electrons at these four  $\mathbf{k}_F$  vectors but will raise the energy of all the other electron pairs, since these other ones are not connected by the same  $\mathbf{Q}$ . For this reason, the Peierls instability does *not* occur in 2D or 3D. [The clearest exposition of this point was written by D. Thouless in a chapter of a book that I read many years ago but which I cannot trace now.]

An exception to this rule – i.e., a vibronic instability - can occur if there is extensive nesting of the Fermi surface, so that there are many pairs of electron states at the Fermi level connected by the same  $\mathbf{Q}$ . But this is not highly likely to just happen by accident, and even if it does in some sense it would be not too different from saying that the dimensionality is effectively reduced.

There has been some confusion about the above point occurs because the so-called cooperative JTE indeed occurs in some real (3D) crystals. The resolution of the conflict is that if the crystal contains molecules or ionic clusters that are sufficiently isolated from one another and from the crystal matrix, JTE can indeed occur in these individual molecules or clusters. If an assembly of such JTE-active molecules or clusters interact weakly with one another, this interaction breaks the original  $\mathbf{P}$  symmetry of the molecule and can align the distortions, leading to collective behavior. Note, though, that cooperative JTE still originates in individual molecules or clusters, while weak inter-molecular coupling merely phase-locks the distortions.<sup>26</sup>

Another possibility for JTE to occur in a crystal is if an electron gets trapped and localized by a defect or self-trapped due to small polaron formation. In this case, again the local  $\mathbf{P}$  symmetry may become relevant and JTE may occur; this possibility will be discussed later in Section 8.

## **6. JTE in polymers and quasi-1D conductors**

For the reasons that should be clear from the previous section, most experts believe that JTE is a “point” or “0D” phenomenon, restricted to molecules and small atomic or ionic clusters, and that it can not occur in periodic systems with extended Bloch-wave states. Nevertheless, I think that there might be an exception to this rule that even most experts are unaware of. Namely, in certain *quasi*-1D systems, such as polymers, extensive *band* degeneracy can occur.<sup>27,28</sup> In this case, the number of (JTE-active) one-electron states that contribute to the vibronic instability can be very large – of the order of the number of atoms, like in the standard JTE.<sup>29,30</sup>

The difference between the Peierls model, which one can classify as 1D, and a polymer, which is *quasi*-1D, is that apart from the translational symmetry along the chain axis common to both cases, the later may have nontrivial, discrete point-group symmetry. Examples are: rotation  $C_n$  around the (vertical) polymer axis, order-two rotation  $U$  around a horizontal axis, vertical and horizontal mirror planes. Also possible are screw axes and glide planes. The spatial symmetry groups of stereo-regular (periodic) polymers are the line groups.<sup>31</sup> They gives rise to quantum numbers such as quasi-momentum, quasi-angular momentum, and parities with respect to mirror symmetry planes.

As a very simple model example, consider a periodic array of benzene rings stacked along the  $z$ -axis and take into account only a single  $\pi$  orbital per C atom. Sixfold-rotation symmetry axis  $C_6$

provides the quantum number  $m = 0, \pm 1, \pm 2, 3$ , the quasi-angular momentum. Any vertical symmetry plane makes  $m = +1$  equivalent to  $m = -1$  and  $+2$  to  $-2$ , hence there will be two doubly-degenerate levels, which we can denote as  $E_{1,-1}$  and  $E_{2,-2}$ . If we allow for some hopping between the neighboring rings, these states will evolve into electron energy bands that carry the same quantum numbers. Hence, there will be two bands,  $E_{1,-1}$  and  $E_{2,-2}$ , doubly-degenerate throughout the Brillouin zone (BZ).

As a real physical example, consider e.g. a single-wall, zig-zag (4,0) carbon nanotube. It has  $L8_4/mcm$  line group symmetry, and every  $k$ -vector has the  $C_{8v}$  point group symmetry.<sup>32</sup> The latter group has some two-dimensional irreducible representations, and as a consequence, in this nanotube some electron bands are two-fold degenerate throughout the Brillouin zone.<sup>32</sup>

Band degeneracy in principle opens a possibility for the *band JTE* – instability of the polymer with respect to a distortion that would split and separate the two bands.<sup>29,30</sup> For this to occur in reality, apart from the band degeneracy it is also necessary that the band is relatively flat, so that  $\Delta E = Q < \psi(-k_F) | \partial U / \partial Q | \psi(k_F) >$  is larger than the bandwidth. However, if the band is too narrow (i.e., if the bandwidth is less than  $k_B T$ ), localization will occur and we are back to 0D.

## **7. $(BeH_2)_x$ band structure, p-JTE**

Long ago, already in late seventies, I have identified a candidate compound for the *band JTE* - a bizarre electron-deficient polymer,  $(BeH_2)_x$ . It has been a favorite of quantum chemists at that time (of punching cards and Kbyte computers) because it only contains few lightest atoms - and because it actually exists, in contrast to other simple model chains frequently studied then.

The  $(BeH_2)_x$  polymer structure is illustrated in Fig. 1. The translational repeat unit of  $(BeH_2)_x$  polymer contains 2 Be and 4 H atoms. The polymer is invariant with respect to the line group  $L4_2/mcm$  which can be generated by an order-four screw axis ( $C_4 | 1/2$ ), two vertical mirror-symmetry planes ( $\sigma_x | 0$ ) and ( $\sigma_y | 0$ ) and a horizontal symmetry plane ( $\sigma_z | 0$ ). The relevant subgroup of the line group  $L4_2/mcm$  is  $L2mc$ , since it leaves the  $k$ -vector invariant and hence its irreducible representations can be used to label the Bloch states and the electron energy bands. Only three of these are relevant here:  $kA_0$ ,  $kA_2$ , and  $kE_{1,-1}$ . In the tight-binding model, it is sufficient to consider only two atomic orbitals,  $|\psi_H\rangle$  and  $|\psi_{Be}\rangle$  and two hopping integrals,  $t = \langle \psi_H | \mathcal{H} | \psi_{Be} \rangle$  and  $t' = \langle \psi_H | \mathcal{H} [C_4 | 1/2] | \psi_H \rangle$ . Using the proper symmetry-adapted linear combinations of atomic orbitals (LCAOs),<sup>27</sup> one can easily calculate the relevant (the lowest three) bands; these are shown in Fig. 2. [More detailed and accurate *ab initio* SCF Hartree-Fock calculations give quite similar bands, plus others above and below.<sup>33,34</sup>]

Apparently, in this model, the highest occupied band  $E_{1,-1}$  is two-fold degenerate throughout the BZ. This may change if we allow the structure to distort. Consider, for example, libration of  $H_2$  units around the  $z$ -axis, one clockwise and the next one counter-clockwise by the same angle. This breaks the screw axis ( $C_4 | 1/2$ ) symmetry, and the line group reduces to  $L2/mcm$  which has no two-dimensional irreducible representations. Hence, the entire  $E_{1,-1}$  band splits into two non-degenerate bands. However, if the  $E_{1,-1}$  band was originally full, this would provide no savings in energy – one band shifts down, the other up by the same amount  $\Delta\epsilon$ , and there is no vibronic instability. However, if the  $E_{1,-1}$  band is partially occupied, the situation is different – after the dis-

tortion, the lower band is full and the upper one is partially filled, hence there is a net energy gain. This will be offset by the elastic restitution force, but for librations this can be relatively weak since there is no change in the length of chemical bonds. So, this would be an example of the band JTE, with very strong *linear* vibronic (libronic!) coupling, because all the electrons in the  $E_{1,-1}$  band would participate.<sup>29,30</sup>

In reality, one could reach this situation by p-type doping, e.g., by replacing some Be by Li. [This has actually been accomplished,<sup>35</sup> as we will expound below.] So, Li-doped  $(\text{BeH}_2)_x$  was my prime candidate for ‘high-temperature’ superconductivity; note that this was happening long before the cuprate revolution and hence to me that meant something like 20 K. I was aware of a major theoretical hurdle, which H. Thomas, who was also interested in this problem, pointed out to me first at some conference in late seventies. [I have learned from Alex that his own thinking was inspired by an early paper of H. Thomas and coworkers,<sup>36</sup> of which I have learned only much later, since it was published in a journal that was not on my reading list.] His killer question was whether indeed the above situation is at all compatible with metallic conduction, or else the carriers would necessarily be localized and immobile. It should be possible to answer this question theoretically, determining more accurately the real electron spectrum of  $(\text{BeH}_2)_x$ , the width of the  $E_{1,-1}$  band, the elastic constants, etc. Experimentally, the question is simply whether Li-doped  $(\text{BeH}_2)_x$  can be made metallic, or it will stay insulating at all doping levels.

## **8. Exps: $(\text{BeH}_2)_x$ crystal, transport**

Indeed, after my theoretical ‘insight’ that  $(\text{BeH}_2)_x$  polymer may be a candidate HTS material, I tried hard to find out what is known experimentally about this material. I was rather surprised (at that time) to find exactly nothing in physics journals. After a substantial effort - at that time I did all my literature search by manually browsing through numerous issues of Physics Abstracts and the Russian Referativnii Zhurnal - I found *one* interesting paper published in ‘Inorganic Chemistry’, in a journal that I certainly did not read regularly. The paper, by Brendel *et al.*,<sup>35</sup> reported a recipe how to prepare crystalline  $(\text{BeH}_2)_x$ . They mixed amorphous polymeric solid  $\text{BeH}_2$  with some Lithium (e.g. 0.5-2.5 mol % of  $\text{LiH}$ ) and then applied compaction-fusion, i.e., exposed the powder to high temperature and pressure for a fixed time interval, then releasing both  $p$  and  $T$ . They explored the phase diagram up to  $p = 12$  kbar and  $T = 250^\circ\text{C}$  (during compaction) and found several crystalline phases, depending on  $p$  and  $T$ . The densest phase ( $0.77 \text{ g/cm}^3$ ) was stable, white to light gray in color. However, in some narrow  $(p, T)$  range the product turned out to be ‘glassy and black’, even though it was indistinguishable from the normal compacted material by chemical analysis, X-ray diffraction, and infrared spectroscopy. There was no evidence of free Be metal, either. They authors speculated about electron delocalization in this metastable phase, which presumably meant that it was indeed metallic. The primary role of Li in this work was to terminate and shorten the  $(\text{BeH}_2)_x$  chains and promote crystallizations. However, in principle this doping could also introduce carriers (holes) in the topmost, two-fold degenerate  $E_{1,-1}$  band.

So, after reading the Brendel *et al.* paper,<sup>35</sup> my interest in  $\text{Li}:(\text{BeH}_2)_x$  increased further. Indeed I would love to try to synthesize this and other light-metal hydrides in thin film form, using powerful COMBE technique and high-throughput testing and characterization that now I have in my hands.<sup>37</sup> I have tried repeatedly to get funding for such experiments, but so far without success.

Nevertheless I am optimistic that the climate in US research administration circles has changed for better and that now there may be a much more benevolent look at efforts to search for superconductivity in new classes of materials hitherto unexplored. Also, in the meantime I have found (thanks to Google and the Web of Science) a little more information on beryllium hydride. It turned out that beryllium hydride is also attractive to people interested in (i) solid rocket propellants, (ii) very efficient moderators (e.g. for making very small nuclear bombs), and (iii) hydrogen storage materials.<sup>38-41</sup> Learning this, I suspect that physical properties of beryllium hydride may have indeed been studied in much detail, even though so little has been published.

## **9. Vibronic coupling in cuprates?**

In relation to superconductivity, clearly we are interested in crystals that are metallic. This implies that there must be sufficient overlap between the relevant atomic orbitals. As we have seen, JTE proper cannot occur in higher dimensions (2D and 3D) but only in molecules or small isolated atomic clusters.<sup>26</sup> The usual story about crystal field splitting of a fivefold-degenerate d level into a threefold-degenerate  $t_{2g}$  and twofold-degenerate  $e_g$  levels, and subsequent further splitting of  $e_g$  due to JTE distortion may apply to an isolated  $\text{CuO}_6$  octahedron, but not to a metal in which electrons occupy extended Bloch orbitals. In fact, in cuprates strong Cu-O hybridization produces a relatively broad ( $\sim 1$  eV) band, judging from Angle-resolved photoemission spectroscopy (ARPES) and Angle-resolved magneto-resistance oscillations (AMRO); in optimally doped and overdoped samples both techniques show nice (although essentially 2D) Fermi surfaces.<sup>42-44</sup> On this side of the phase diagram, there are other signs of decent Fermi-Liquid behavior, such as decent Wiedeman-Franz-law behavior.

At low doping levels, the situation may be different; specifically below the metal-to-insulator crossover at  $x_c \approx 0.05$  one could imagine that electron localization may occur, in which case one should not be surprised to detect concomitant local lattice distortion (cuprates are essentially ionic crystals!), and even perhaps JTE. If this indeed happens, polaron or bipolaron formation may play the key role.<sup>45-47</sup> But to say the truth, I have not understood yet what causes this crossover in the first place – the jury is still out. In manganites the situation may be a bit clearer, with some typical signatures of both large and small polaron behavior (at low and high temperature, respectively).<sup>48-50</sup>

As for the immediate future, in my group at Brookhaven National Laboratory we have mastered the technique of growing quite reproducibly atomically smooth and perfect HTS films, in particular of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  with doping level ranging from  $x = 0$  to  $x = 0.50$ . This indeed opens the door to many interesting experiments some of which are already well on track. I hope that before long, on the scale of months, we will be able to announce results that will shed some new light on the great cuprate puzzle, and Alex will rejoice.

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## **Appendix. Karl-Alex Mueller: a personal touch**

I first met Alex at Ted Geballe's beautiful estate in Woodside, CA (not far from Stanford) exactly 20 years ago, in the spring of 1987. The party started early in afternoon and lasted till late in the night. Pierre-Gilles de Gennes, whom I already knew from his earlier visits to (what was then) Yugoslavia, was also present. He and several other guests succumbed to the temptation of the sunny California day to swim in the large pool. We did not know that two in the company were to become Nobel laureates subsequently, Alex by the end of the same year, and Pierre-Gilles four years later. But at this party they were still mortals and I used the chance to bug them with some physics. I found soon enough that Alex nourishes strong opinions (to borrow Nabokov's phrase). I guess I do as well, so our conversation appeared more like a debate. We have continued discussing in the same spirit on several other occasions – I remember well our long walks and talks in snow (which didn't seem to bother Alex at all) in Closters, Switzerland, as well as several private dinners in warmer places such as Los Alamos and Santa Fe, and elsewhere. Even though our opinions are rarely identical (as I am afraid this article testifies), Alex has never ceased to impress me with his lucidity and logic – apart from his physics intuition, which no one can question. And then there is his infectious enthusiasm – he cares about physics a lot, it is his great passion.

Another seems to be fast cars. My favorite K.-A. Mueller anecdote is that he actually *drove* from Zurich to Bremen and back – I guess about  $10^3$  kilometers one way – just to visit my laboratory, see my MBE system, and discuss physics. [True, he was still young then – only 73!] Actually, he tried – and succeeded, his enthusiasm was infectious – to convince me to try to reproduce the result of a group from Japan who claimed to have seen the giant proximity effect (GPE) in Josephson junctions with  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  (LSCO) electrodes and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  barrier,<sup>51</sup> both polaronic materials according to Alex. I indeed tried – but failed; we saw no supercurrent whatsoever, even with very thin manganites barriers. This of course did not prove much – there are many ways in which one can make a bad junction, and hence I have never published this. We got one possibly interesting result from our attempts to reduce the lattice mismatch and improve the epitaxy by reducing the La content. Eventually I tried using pure  $\text{SrMnO}_3$ , although I could not find any information about its bulk lattice constants. I e-mailed to several expert friends and two, Ted Geballe and Darrell Schlom, responded promptly that  $\text{SrMnO}_3$  is actually hexagonal. But thanks to the nine-hour time-zone difference the experiment was already underway and I actually observed excellent hetero-epitaxy. We synthesized  $\text{SrMnO}_3$  in perovskite structure, pseudomorphic to LSCO, by virtue of epitaxial strain and stabilization. However, this perovskite  $\text{SrMnO}_3$  did not transmit supercurrent, so we never published this result either, although I did show it at the MRS Meeting later the same year and couple other conferences. Subsequently other groups published the same result. We followed this line of investigation by trying other candidate compounds and eventually succeeded to demonstrate GPE using underdoped LSCO as the barrier material.<sup>52</sup>

Recently, Alex has suggested to me another exciting idea that I cherish and indeed intend to put to experimental test as soon as possible. Maybe this time I will be luckier – future will tell.

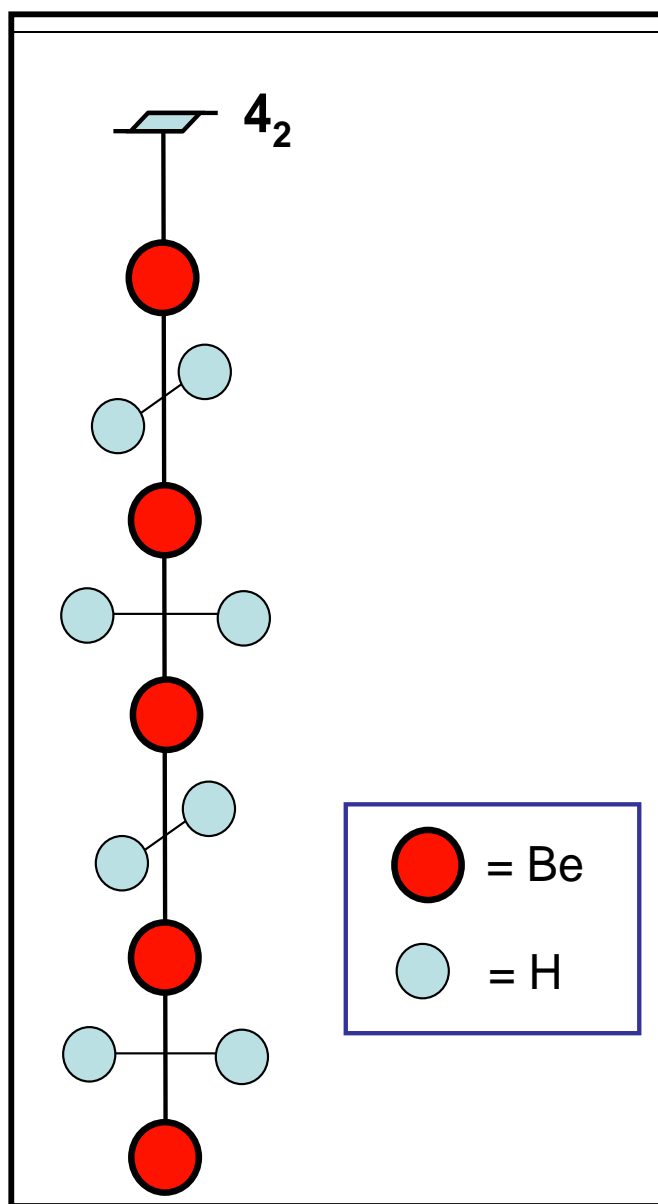


Fig. 1. A model of  $[\text{BeH}_2]_x$  polymer. The line group is  $\mathbf{L}4_2/\text{mcm}$ .

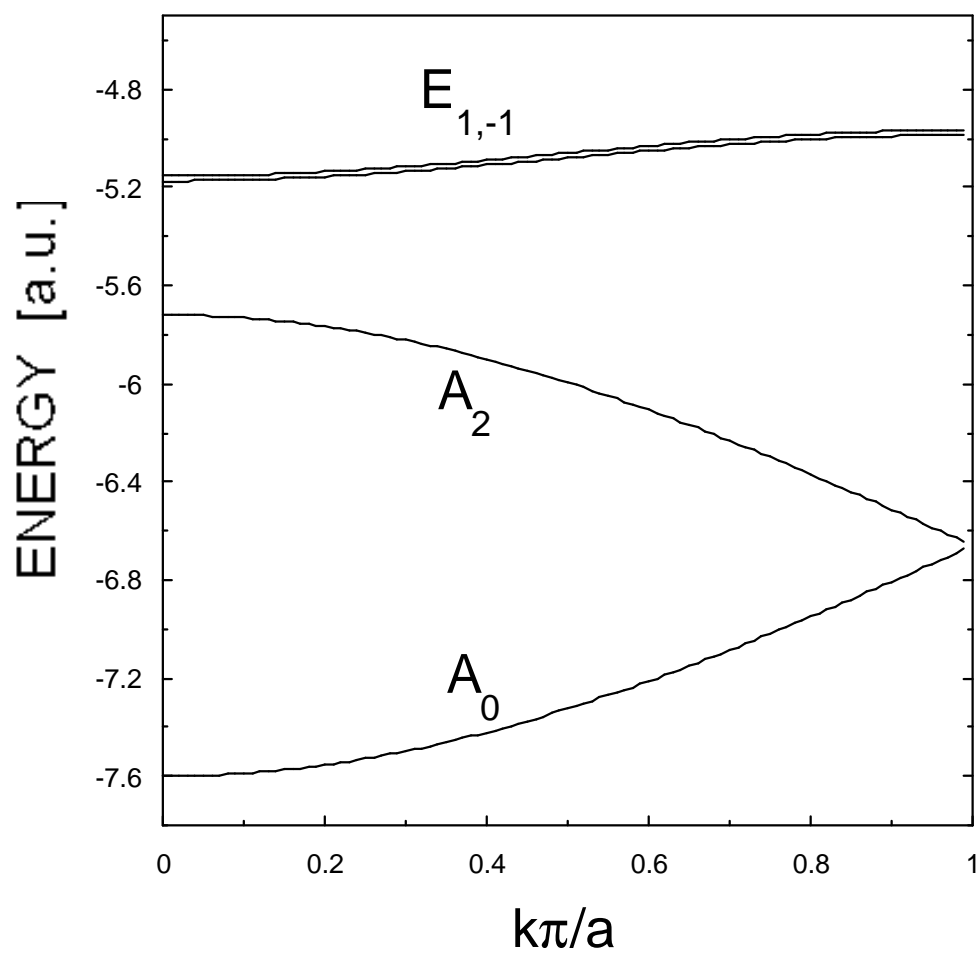


Fig. 2. Simplified tight-binding band structure of  $[\text{BeH}_2]_x$  polymer. Note that the  $E_{1,-1}$  band is twofold degenerate throughout the Brillouin zone. It is fully occupied in  $[\text{BeH}_2]_x$  but could be made partially occupied by e.g. Li doping.

in *High  $T_c$  Superconductors and Related Transition Metal Oxides, Special Contributions in Honor of K. Alex Müller on the Occasion of his 80th Birthday*, A. Bussmann-Holder, H. Keller, Eds., (Springer Verlag, 2007).



Fig. 3. April 21, 2006 at the house of Leilani and Steve Conradson (standing left, with their son in between): the celebration of Alex's 79<sup>th</sup> birthday. Seated, left to right: Davor Pavuna, Takeshi Egami, Alex, and Hugo Keller. Standing right: Natasha and Ivan Bozovic. Missing in the picture is Dragan Mihailovic who took this photo.